Section 9

ETHYL TERTIARY BUTYL ETHER (ETBE)

Quick Reference Data

Oxygenate Blending Properties at 2.7 Weight % Oxygen
(Base Fuel of 87.6 AKI, 9.0 Sensitivity, and an RVP of 8.1 psi)

	MON	RON (R+M)/2	AKI	Sensitivity (R-M)	RVP (psi)
MTBE	99	113	106	167	9
ETBE	103	119	111	13.8	3
Ethanol	99	126	113	27.2	20

Requirements to Make 1 Gallon of:

	Isobutylene	Alcohol
ETBE	.68	.42
MTBE	.79	.34

Current Production Capacity

MTBE	1.1 Billion Gallons/Yr. (75 mB/d)
ETBE	None

In order to meet the Clean Air Act requirements for cities that do not attain EPA's carbon monoxide requirements, gasoline must contain 2.7% oxygen by weight. If ETBE is used as the oxygenate to satisfy this requirement, each gallon of gasoline would need to contain 17.2% ETBE by volume.

The U.S. Treasury recently approved the use of the federal alcohol fuel tax credit for ethanol used in the production of ETBE. While ETBE is not yet commercially available in large quantities, a few ETBE production facilities are now planned by industry. Given the high degree of similarity in the production processes used to make MTBE and ETBE, it is also possible that MTBE production facilities could be converted to produce or coproduce ETBE.

Useful Terms and Definitions (also see Glossary)

- **Aromatics:** high octane blending components that have a benzene ring in their molecular structure. Commonly used term for the BTX group (benzene, toluene, xylene). Aromatics are hydrocarbons.

- **Azeotrope**: a liquid mixture that is characterized by a constant minimum or maximum boiling point which is different than that of any of the components. Azeotropes distill without change in composition.

- **Distillation Curves:** the reference to plotting a line connecting the percentages of gasoline that evaporate at various temperatures. Distillation curve is used as an important control for fuel volatility (vaporization) standards.

- **Hydrocarbon:** a compound composed of carbon and hydrogen atoms.

- **Octane Number (Rating):** a measurement term used to identify the ability of a fuel to resist spontaneous combustion; the lower the octane rating the greater the tendency for a fuel to prematurely ignite due to heat and compression inside the cylinder and cause engine "knock."

  - ***Motor Octane:*** the octane as tested in a single cylinder octane test engine at more severe operating conditions. Motor Octane Number (MON) affects high speed and part throttle knock and performance under load, passing, climbing hills, etc. Motor Octane is represented by the designation M in the (R+M)/2 equation and is the lower of the two numbers.

  - ***Pump Octane:*** a term used to describe the octane as posted on the retail gasoline dispenser as (R+M)/2 and is the same as Antiknock Index.

  - ***Research Octane:*** the octane as tested in a single cylinder octane test engine operated under less severe operating conditions. Research Octane Number (RON) affects low-to-medium speed knock and engine run-on. Research Octane is represented by the designation R in the (R+M)/2 equation and is the higher of the two numbers.

- **Reid Vapor Pressure (RVP):** a method of determining vapor pressure of gasoline and other petroleum products. Widely used in the petroleum industry as an indicator of the volatility (vaporization characteristics) of gasoline.

- **Volatility:** term used to describe a gasoline's tendency to change from liquid to vapor.

Key Issues and Implications

Issue # 1: ETBE is a high octane, low volatility oxygenate

Ethers (like ETBE) and heavier alcohols (such as **tertiary butyl alcohol (TBA)) are** oxygenates **characterized by low volatility (low blending RVP), high octane, and provide some beneficial** cosolvency **effects that could be used by refiners to correct the blending RVP of low molecular weight alcohols.**

Implications of ETBE's High Octane Low Volatility:

- Lower VOC and evaporative emissions which will reduce smog and ozone formation.
- Lower tailpipe emissions (CO) due to presence of oxygen in the blend.
- Reduction of tailpipe HC emissions due to more complete combustion of the fuel blend.
- Reduction in toxic emissions due to substitution of ETBE for benzene and aromatics while maintaining high octane.
- Lower RVP contributes to cold start driveability problems. Tests conducted by Phillips Petroleum found that cold start driveability was not noticeably affected by as much as 23.5% by volume (equivalent of 3.7% O_2 by weight).

Detailed Information: Refer to pages 9-3 through 9-6.

Issues and Implications

Issue #2: *Compatibility with existing liquid fuels infrastructure.*

ETBE, unlike alcohols, has a relatively low solubility in water. Because of this advantage, ethers (like ETBE and MTBE) can be blended into gasoline at the refinery and shipped to the market through common carrier gasoline pipelines.

Implications of compatibility with existing infrastructure:

- ETBE can be shipped via existing product pipelines, tank trucks, etc.
- Petroleum refiners will accept ETBE just as they accept MTBE, as a blending stock for reformulated gasoline.
- ETBE is completely soluble in base gasoline (even in the presence of water) and can, therefore, be splash blended at terminals.
- Presence of ETBE in gasoline requires no engine or vehicle modifications since it has none of the corrosion or material incompatibility qualities of ethanol or methanol.

Detailed Information: Refer to pages 9-3 through 9-6.

Section 9

ETHYL TERTIARY BUTYL ETHER (ETBE)

- Introduction
- Gasoline related properties
- Performance
- Production process technology
- Supplies and commercialization
- Conclusion

Introduction

The technical feasibility and application of methanol, ethanol, tertiary butyl alcohol (TBA), and methyl tertiary butyl ether (MTBE) in motor fuels has been extensively investigated during the last two decades [1-10]. Of the possible oxygenated fuels, the two most common in use today are MTBE and ethanol. However, because of the relative scarcity of future low-priced, domestically produced methanol for MTBE and the likely trend toward lower volatility gasolines, ethyl tertiary butyl ether (ETBE) has emerged as a "best fuel" blending candidate for the future. This section discusses the blending properties, performance properties, and the process technology to produce ETBE, as compared to its two competitors: MTBE and ethanol.

Gasoline related properties

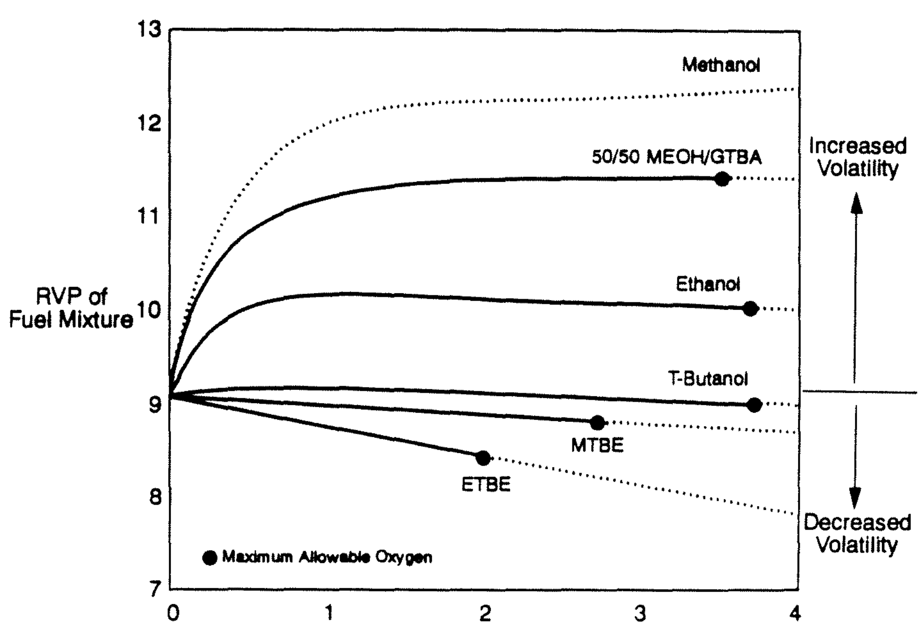
The typical properties for oxygenates are shown in Table 9-1. [11] Ethers have superior fuel blending properties when compared to the original alcohol forms. The blending RVPs (Reid Vapor Pressure) of most alcohols are much higher than their true vapor pressures, as shown in Table 9-1 and Fig. 9-1 [12]. The RVP increase is due to the unfavorable interreaction between the very polar hydroxyl group of alcohols and the non-polar hydrocarbons, leading to the formation of azeotropes. This tendency of the

TABLE 9-1. GASOLINE RELATED PROPERTIES OF OXYGENATES

PROPERTY	ETHERS			ALCOHOLS			GASOLINE
	ETBE	MTBE	TAME	TBA	ETOH	MEOH	
Boiling Point (°F)	161	131	187	181	173	148	80-437
Freezing Point (°F)	-137.2	-164	-	78.0	-173.2	-143.5	-40.0
Vapor Pressure:							
Neat RVP (100°F)	4.0	7.8	2.5	1.7	2.3	4.6	8-15
Blending RVP	4.0	8.0	2.0	9.0	17.0	31.0*	
Octanes:							
Blending (R+M)/2	111	110	105	100	115	108*	
Water Solubility (Wt%)							
Water in Fuel	0.6	1.4	-	∞	∞	∞	Negligible
Fuel in Water	2.0	4.3	0.6	∞	∞	∞	Negligible
Density (lb/gal @ 60°F)	6.2	6.2	6.4	6.6	6.6	6.6	6.0-6.5
Energy Density (LHV)							
MBTU/Gal	96.9	93.5	100.6	94.1	76.0	56.8	109.0-119.0
MBTU/lb	15.5	15.1	15.7	14.3	11.5	8.6	18.0-19.0
Latent Heat of Vaporization (60°F):							
MBTU/Gal	0.83	0.86	0.90	1.70	2.38	3.34	~0.90
MBTU/lb	0.13	0.14	-	0.26	0.40	0.51	~0.15
Oxygen Density Vol. % @ 2.7 Wt% Oxygen	17.2	15.0	16.7	11.8	7.3	5.1	0.0
Azeotropes with Hydrocarbons	No	No	No	Yes	Yes	Yes	No

* Properties of Methanol/Cosolvent Blends
∞ Infinite

Figure 9-1
RVP Effects of Adding Oxygenates to 9 RVP Fuels



volatility of alcohol/gasoline blends to increase is common only with low molecular weight alcohols, such as methanol and ethanol.

Policy Issue #1

> Ethers (like ETBE) and heavier alcohols (such as tertiary butyl alcohol (TBA)) are oxygenates characterized by low volatility (low blending RVP), high octane, and provide some beneficial cosolvency effects that could be used by refiners to correct the blending RVP of low-molecular weight alcohols.

This is illustrated in Fig. 9-1, by the suppression of methanol's RVP increase when it is mixed with GTBA (gasoline grade tertiary butyl alcohol).

Table 9-1 and Fig. 9-1 also show that ETBE has a vapor pressure advantage over ethanol or even MTBE. At the 2.0 weight percent oxygen level, ETBE has 1.5 psi lower RVP than ethanol and 0.5 psi lower RVP than MTBE. This advantage increases as the oxygen level increases. At the 3.0 level, ETBE has a 1.8 psi lower RVP than ethanol and a 0.8 psi lower RVP than MTBE. When used in gasoline, this allows the use of more butane and other desirable low-cost blend stocks, without RVP penalty. [13]

Low-molecular weight alcohols are infinitely soluble in water. This property is a major drawback to the development of methanol and ethanol as gasoline components because of their phase separation in the presence of water.

Policy Issue #2

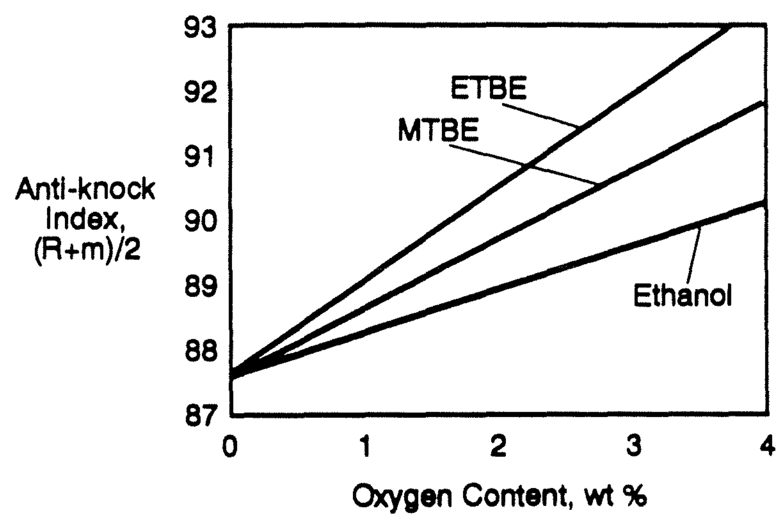
> ETBE, unlike alcohols, has a relatively low solubility in water. Because of this major advantage, ethers (like ETBE) can be blended to gasoline at the refinery and shipped to the market through common carrier gasoline pipelines.

Ether/gasoline blends do not experience the problem of phase separation. Ethers are even used to improve the water tolerance of alcohol/gasoline blends.

Performance

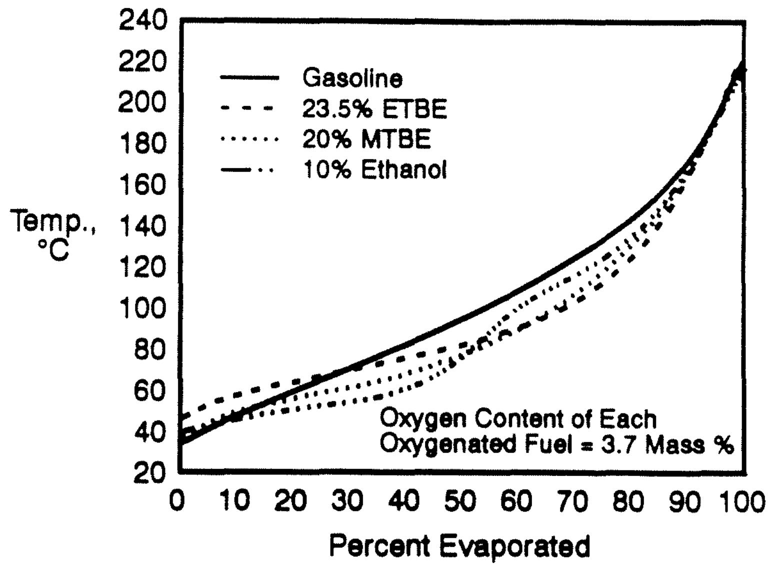
ETBE has a significantly higher Motor Octane Number (MON) Boost, or anti-knock ratio, than either of ethanol or MTBE. This is expected to enhance vehicle performance since most of today's smaller, higher performance engines operate at higher engine speeds which is more closely represented by the operating conditions of the ASTM Motor Octane Method. Figure 9-2 [14] shows the effect of the oxygenates on anti-knock index as a function of oxygen content.

Figure 9-2
Oxygenate Effect on Anti-knock Index



Alcohols form azeotropes with hydrocarbons, ethers do not. The azeotrope reduces the boiling points in some regions of the gasoline distillation curve, as shown in Figure 9-3. [15] Which part of the curve is affected depends on the boiling point and the type of oxygenate used. The lighter alcohols such as methanol and ethanol form minimum boiling point azeotropes with hydrocarbons and produce a substantial increase in the front-end volatility of the distillation.

Figure 9-3
Effects of ETBE, MTBE, and Ethanol at Equal Oxygen Content, on the Distillation Characteristics of Gasoline

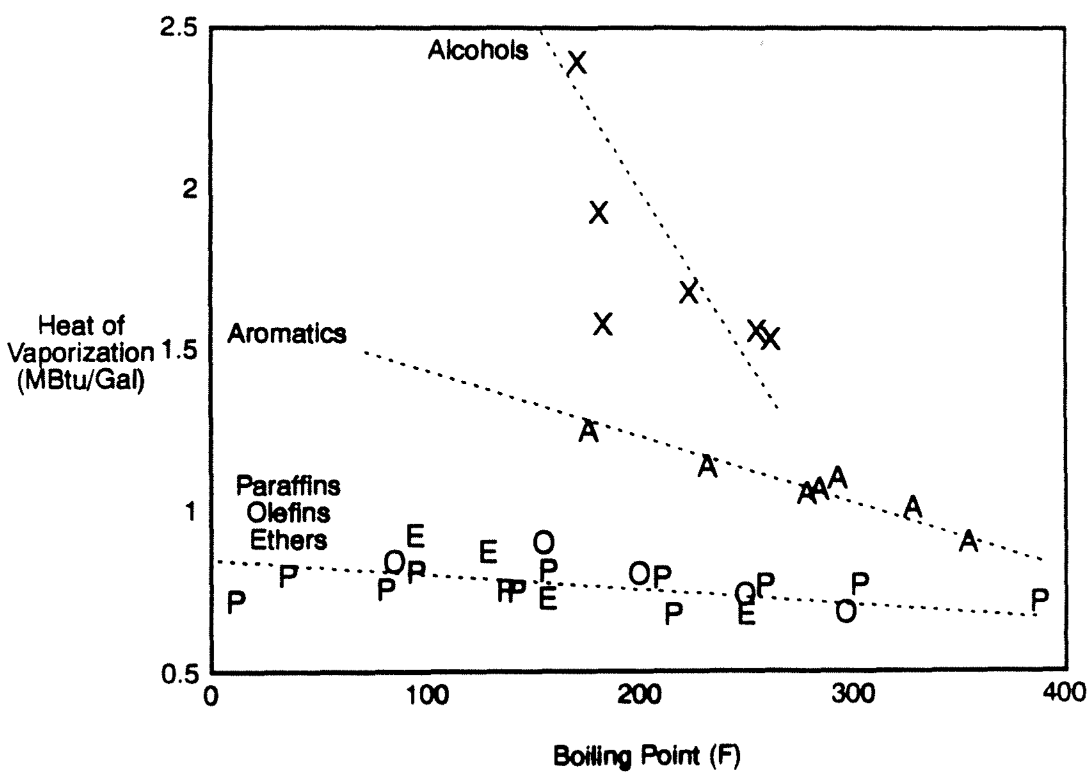


Since ethers do not form azeotropes with hydrocarbons, ETBE produces a more favorable increase in the mid-range volatility of the gasoline. This helps improve the "cold driveability" index of gasoline by lowering the 50% point of gasoline, as illustrated in Fig. 9-3.

Both alcohols and aromatics have a significantly higher heat of vaporization (Hv) requirement, but alcohols have the advantage of a lower boiling point. Ethers have a low Hv, independent of their boiling points, as shown in Figure 9-4. [16] During cold engine operation, the fuel vaporization process super-cools the air since there is no other source to draw heat from. Fuels with both a high Hv and a high boiling point, such as aromatics (xylene, toluene, benzene), will be the most difficult to vaporize because they super-cool the air. A poor vaporization leads to poor fuel/air mixing which contributes to incomplete combustion (higher HC emissions). To avoid this problem, General Motors (GM) has suggested reducing the 90% point temperature of the gasoline distillation curve by removing the back end (high boiling portion) of the fuel and increasing the mid-range volatility of the fuel. This can be accomplished by the blending of ETBE with gasoline. [17] Previous studies by others have also shown that increasing mid-range volatility will reduce HC emissions from the tailpipe. [18] These results confirm the expected beneficial effect of ETBE on the gasoline distillation curve.

ETBE's low boiling point also has the added benefit of putting more of the octane into the front end of the distillation curve. This produces a better octane distribution through the full boiling range of the gasoline and provides added performance during high RPM engine operation.

Figure 9-4
Heat of Vaporization of Oxygenates and Hydrocarbons



Although the use of ETBE in gasoline is currently limited to 12.7 volume percent (2.0 weight percent oxygen) by the EPA's "gasoline substantially similar rule," studies were performed with levels of ETBE ranging from 0.0 to 23.5 volume percent (3.7 weight percent oxygen) in gasoline. The obtained results show that cold start driveability was not found to be noticeably affected by as much as 23.5 percent ETBE. No considerable detrimental effects were observed due to corrosion of typical materials found in fuel systems. The swelling of polymeric and elastomeric parts of the fuel systems was shown to be no greater than with typical fuels in current use.

Production process technology

Figure 9-5 [19] shows the simplified flow chart for the production of ETBE and MTBE, by a catalytic reaction between isobutylene and ethanol or methanol, respectively. A mixture of C_4 feedstock from fluid catalytic cracking unit (FCCU), is combined with ethanol or methanol in a controlled optimized ratio to isobutylene. The resulting mixture is fed to the liquid-phase, fixed-bed ETBE or MTBE reactor, containing an ion exchange resin catalyst. The typical composition of the C_4 stream from FCCU is shown in Table 9-2, while the composition of the product stream is illustrated in Table 9-3. [20] The C_4 feedstock can also be obtained from the by-product isobutylene from olefin plants and from isobutane dehydrogenation plants.

Figure 9-5
Flow Chart of MTBE/ETBE Process

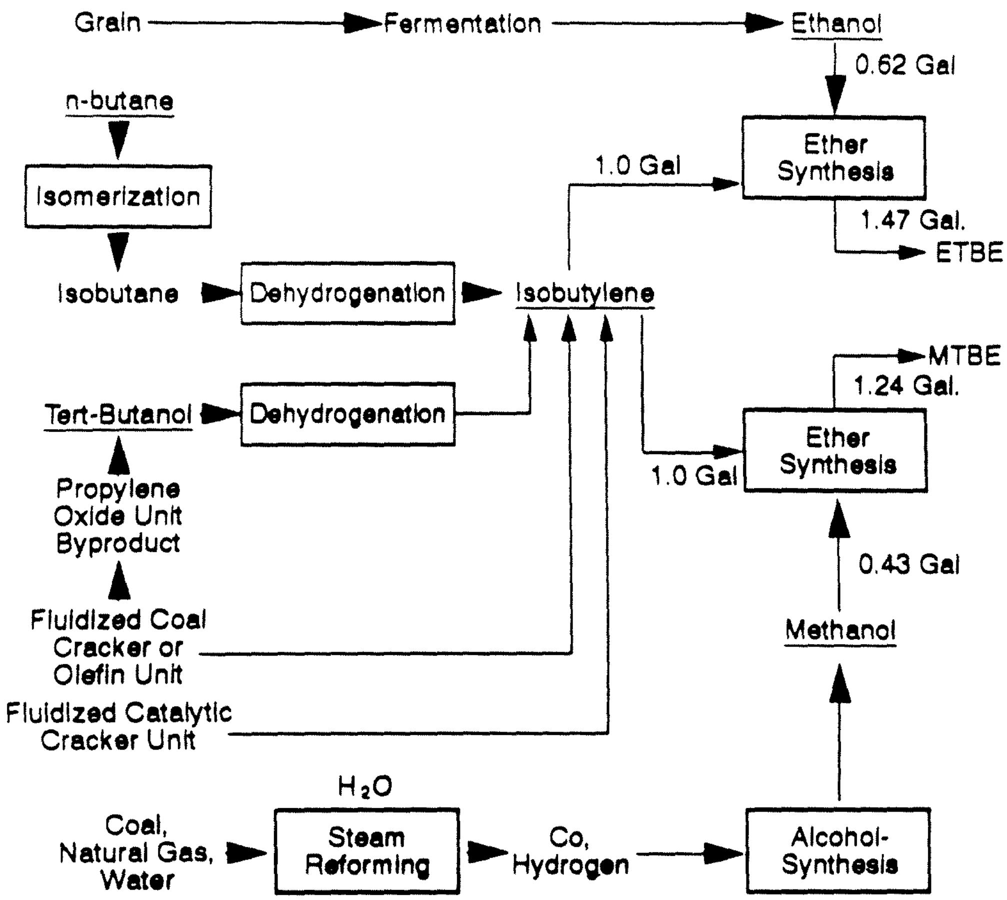


TABLE 9-2. CHARGE STOCK COMPOSITION

FCCU C_4 STREAM

Component	BPSD
Isobutane	2,296
Isobutylene	959
Butene-1	905
Normal Butane	931
TR-Butene-2	1,102
CIS-Butene-2	676
Pentanes	89
	6,958

ETHANOL STREAM

COMPONENT	BPSD
Ethanol	485
Water	32
	511*

* CH_3CH_2OH-H_2O Solutions have a negative mixing volume.

TABLE 9-3. PRODUCT STREAM COMPOSITION

C. STREAM RETURNED TO REFINERY FOR ALKYLATION CHARGE OR OTHER

Component	BPSD
Isobutane	2,296
Isobutylene	35
Butene-1	905
Normal Butane	931
TR-Butene-2	1,102
CIS-Butene-2	676
Pentanes	89
Diethyl Ether	2
	6,036

TBA PRODUCT

COMPONENT	BPSD
ETBE	10
TBA	133
Other C-8's	79
Water	1
	233

ETBE PRODUCT

COMPONENT	BPSD
Diethyl Ether	2
ETBE	997
TBA	1
	1,000

The chemical reactions that occur and the volumetric yield equations are shown in Table 9-4. [21] In addition to the main reaction producing MTBE and ETBE, side reactions occur that produce, in addition to tertiary butyl alcohol (TBA) and diisobutylene (DIB), a small amount of diethyl ether (DEE).

TABLE 9-4. ETBE AND MTBE REACTIONS

Main Reaction

$$CH_2C(CH_3)_2 + CH_3CH_2OH \longrightarrow (CH_3)_3COCH_2CH_3$$

$$CH_2C(CH_3)_2 + CH_3OH \longrightarrow (CH_3)_3COCH_3$$

Side Reactions	Typical Concentrations
1. $2iC_4^= \longrightarrow DIB$	<.1%
2. $iC_4^= + H_2O \longrightarrow TBA$	2.0%
3. $2\ CH_3\text{-}CH_2OH \longrightarrow CH_3\text{-}CH_2\text{-}O\text{-}CH_2CH_3 + H_2O$ Diethyl Ether	<.02%

Volume Yield Equation

$$1.0iC_4^= + 0.62\ ETOH = 1.46\ ETBE$$

$$1.0iC_4^= + 0.43\ MeOH = 1.27\ MTBE$$

An isobutylene conversion level of as high as 96% for ETBE or MTBE is achieved. However, significant amounts of alcohol are found in the bottoms product (ETBE/MTBE). Because of both the azeotropic properties of alcohols and the distribution problems due to their phase separation, an ethanol/methanol recovery system is included in the design in order to produce high purity ETBE/MTBE suitable for the merchant market and pipeline distribution systems. The ether/alcohol mixture is fractionated in an alcohol extractor where the alcohol is contacted counter currently by a circulating wash water stream leaving this extractor containing less than 100 ppm of ethanol. The circulating wash water with absorbed ethanol flows from the bottom of the extractor to the ethanol stripper where the ethanol is recovered as an overhead product and recycled to the ETBE reactors. Although the water content of this ethanol stream poses no problem to the reaction catalyst, an additional amount of TBA is produced.

The catalyst used in the process is sensitive to poisoning by organic and inorganic bases, nitrogen compounds and trace metals, all present in the feedstocks. The catalyst activity decays at a rate proportionate to the level of feedstock impurities. The catalyst life can be extended to two years or more, depending on the type of design and technology involved. Conversion in a well-run operation can be maintained for a 2-year period. [22]

Supplies and commercialization

As mentioned earlier, the two oxygenated fuels most used today are MTBE and ethanol. ARCO Chemical Company, which completed the construction of its first MTBE plant in December of 1979, is the largest producer in the world with a total capacity for MTBE of over 2.5 million metric tons per year.

It has been suggested that the main constraint to future use of ethers in the gasoline pool will be the availability of isobutylene to react with ethanol or methanol. If this is the case, ETBE will enjoy an added advantage over MTBE in that less isobutylene is required to react with ethanol on a per gallon basis, i.e., 0.68 gallons isobutylene for 1 gallon of ETBE vs. 0.79 gallons of isobutylene for 1 gallon of MTBE. On the other side of the equation, more ethanol than methanol is required to make equivalent amounts of ETBE and MTBE, respectively. This presents no problems since ethanol is and will be an abundant, domestically produced fuel or feedstock. This is very important in light of national security concerns, especially when estimates of future methanol supplies predict that the majority of sources will be from either the Middle East or the USSR.

The economics for ETBE have not been completed yet and until the process is completely proven, current economics favor the production of MTBE. However, the technology exists to produce ETBE at such time as conditions warrants. Now that the U.S. Treasury has approved the use of the federal alcohol fuel tax credit for ethanol used in the production of ETBE, this opens an economical route for ethanol to go into gasoline in the form of a hydrocarbon-like ether.

Conclusions

ETBE is a potentially valuable blending stock for gasoline. Because it can be produced from isobutylene and agriculturally (grain or biomass) based ethanol, tax incentives have been created to increase its economic viability. Experimental studies at concentrations of up to 23.5 volume percent did not show any "fatal flaw." Based on overall properties and performance, ETBE, a new blending component in gasoline and useful octane enhancer, was evaluated comparable or even better to those of the base gasoline, ethanol and MTBE. [23]

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